

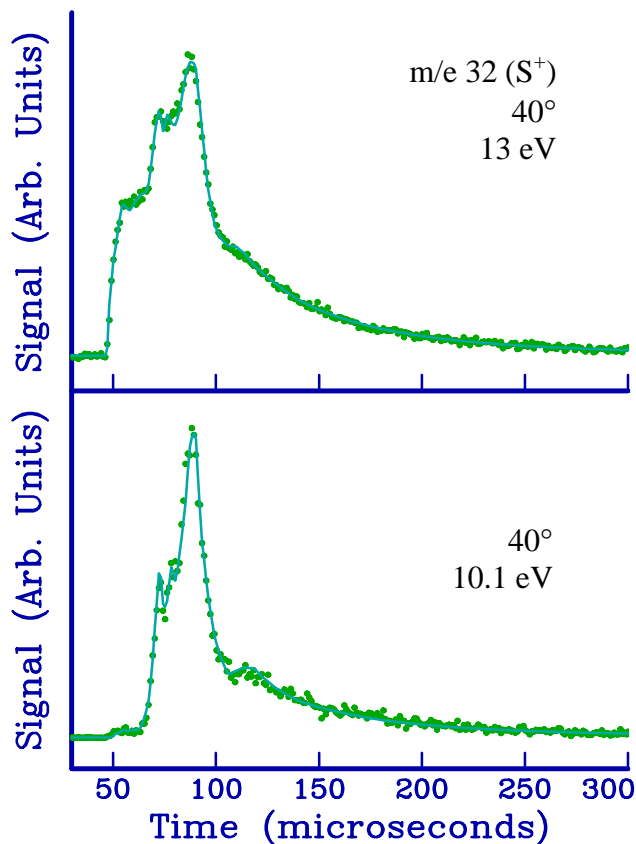
Electronic Branching and Correlated Distributions in Molecular Photodissociation

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The study of multistate photodissociation is an important ongoing area of study in chemical dynamics. There are numerous techniques that allow the selective detection of specific electronic states of photofragments. These techniques permit the measurement of correlated state distributions that can provide detailed information about the excited state potential energy surfaces on which a dissociation evolves. However, many of these methods sacrifice velocity resolution for state-selectivity and are often limited to probing only a subset of the final products. Traditional photofragment translational spectroscopy (PTS) experiments, utilizing electron impact for product ionization, provide high velocity resolution and permit the study of all possible reaction products. The ‘universal detection’ capability of electron impact PTS is critical to investigations of complex reaction mechanisms and large polyatomic systems. The utilization of synchrotron radiation from the Advanced Light Source (Beamline 9.0.2.1) for product ionization allows the experimentalist to choose between either selective detection, based on electronic states or internal energy, or universal detection.



The photodissociation of CS₂ provides the first demonstration of state-selective detection using VUV ionization on this apparatus. Upon excitation at 193 nm, CS₂ dissociates *via* two different channels, resulting in CS and either S(³P) or S(¹D) products. As a benchmark molecule, the photodissociation has been studied previously by many groups, and the S(³P)/S(¹D) branching ratio and the correlated state distributions have been the subject of debate and conflicting reports. Utilizing PTS with synchrotron photoionization, we have discriminated against the S(³P) products, allowing the state-selective detection of the S(¹D) products. Figure 1 shows two time-of-flight (TOF) spectra for m/z 32 (S⁺) as a function of the photoionization energy. At 13.0 eV, both electronic states of sulfur are ionized. The resulting translational energy distribution is shown in the upper panel of Figure 2, which is similar to previously determined distributions from electron impact studies. At 10.1 eV, only the S(¹D) electronic state can be ionized, allowing the direct determination of the vibrationally resolved translational energy distribution of the CS + S(¹D) channel. The lower panel of Figure 2 shows the measured translational energy distribution

for the $\text{CS} + \text{S}(^1\text{D})$ channel. The spatial anisotropy of the angular distribution for each product channel was also determined and suggested that the two channels have similar origins and that the electronic branching may be decided at point further along the dissociation coordinate. By simulating the vibrational distribution, we find that the partitioning of the vibrational energy peaks at $v = 3$.

The ability to directly measure single electronic states using PTS can provide a detailed view of complicated multistate photodissociation processes and should allow the photochemistry of atmospherically relevant molecules to be studied in significant detail.

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